Claims

1) Polymer microparticles dispersed in an aqueous phase and with a fully crosslinked exterior, obtainable by a multistage polymerization process which involves conducting

a) in a first step, an aqueous-phase polymerization of a monomer mixture comprising

i) from 7.5 to 93% by weight of at least one ethylenically monofunctional compound;

ii) from 0.3 to 47.5% by weight of at least one ethylenically difunctional or polyfunctional compound;

in the presence of a polymer selected from a

- polyesterpolyol having a number-average molecular weight of from 500 to 10 000, an acid number of between 22 and 224, and an OH number of between 60 to 400;
- polyurethane having a number-average molecular weight of from 500 to 20 000, an acid number of between 25 and 150, and an OH number of between 50 to 350, said polyurethane containing on average per molecule at least one free carboxyl group originating from a polyesterpolyol; and/or
- polyacrylate having a number-average molecular weight of from 2 000 to 100 000, an acid number of between 25 and 300, and an OH number of between 50 to 250;

b) in a subsequent step, a reaction of the product obtained from step a) with

iii) from 5 to 85% by weight of at least one ethylenically monofunctional compound;

the sum of the fractions of components (i) to (iii) being 100% by weight;

followed by a reaction of the product obtained from step b) with a crosslinker.

2) A polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, obtainable by a multistage polymerization process which involves conducting

a) in a first step, an aqueous-phase polymerization of a monomer mixture comprising

i) from 15 to 95% by weight of at least one ethylenically monofunctional compound;

in the presence of a polymer selected from a

- polyesterpolyol having a number-average molecular weight of from 500 to 10 000, an acid number of between 22 and 224, and an OH number of between 60 to 400;
- polyurethane having a number-average molecular weight of from 500 to 20 000, an acid number of between 25 and 150, and an OH number of between 50 to 350, said polyurethane containing on average per molecule at least one free carboxyl group originating from a polyesterpolyol; and/or
- polyacrylate having a number-average molecular weight of from 2 000 to 100 000, an acid number of between 25 and 300, and an OH number of between 50 to 250;

b) in a subsequent step, a reaction of the product obtained from step a) with

ii) from 2.5 to 83% by weight of at least one ethylenically monofunctional compound;

iii) from 0.1 to 42.5% by weight of at least one ethylenically difunctional or polyfunctional compound;

the sum of the fractions of components (i) to (iii) being 100% by weight;

followed by a reaction of the product obtained from step b) with a crosslinker.

3. A polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, obtainable by a multistage polymerization process which involves conducting

a) in a first step, an aqueous-phase polymerization of a monomer mixture comprising

i) from 7.5 to 93% by weight of at least one ethylenically monofunctional compound;

ii) from 0.3 to 47.5% by weight of at least one ethylenically difunctional or polyfunctional compound;

in the presence of a polymer selected from a

- polyesterpolyol having a number-average molecular weight of from 500 to 10 000, an acid number of between 22 and 224, and an OH number of between 60 to 400;
- polyurethane having a number-average molecular weight of from 500 to 20 000, an acid number of between 25 and 150, and an OH number of between 50 to 350, said polyurethane containing on average per molecule at least one free carboxyl group originating from a polyesterpolyol; and/or
- polyacrylate having a number-average molecular weight of from 2 000 to 100 000, an acid number of between 25 and 300, and an OH number of between 50 to 250;

b) in a subsequent step, a reaction of the product obtained from step a) with

iii) from 2.5 to 83% by weight of at least one ethylenically monofunctional compound;

(iv) from 0.1 to 42.5% by weight of at least one ethylenically difunctional or polyfunctional compound;

the sum of the fractions of components (i) to (iv) being 100% by weight;

followed by a reaction of the product obtained from step b) with a crosslinker.

4) A polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, obtainable by a multistage polymerization process which involves conducting

a) in a first step, an aqueous-phase polymerization of a monomer mixture comprising

i) from 15 to 95% by weight of at least one ethylenically monofunctional compound;

in the presence of a polymer selected from a

- polyesterpolyol having a number-average molecular weight of from 500 to 10 000, an acid number of between 22 and 224, and an OH number of between 60 to 400;
- polyurethane having a number-average molecular weight of from 500 to 20 000, an acid number of between 25 and 150, and an OH number of between 50 to 350, said polyurethane containing on average per molecule at least one free carboxyl group originating from a polyesterpolyol; and/or
- polyacrylate having a number-average molecular weight of from 2 000 to 100 000, an acid number of between 25 and 300, and an OH number of between 50 to 250;

b) in a subsequent step, a reaction of the product obtained from step a) with

ii) from 5 to 85% by weight of at least one ethylenically monofunctional compound;

the sum of the fractions of components (i) and (ii) being 100% by weight;

followed by a reaction of the product obtained from step b) with a crosslinker.

5) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in claim 3, characterized in that the ethylenically difunctional or polyfunctional compound in steps a) and b) is the same.

6) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in claim 3, characterized in that the ethylenically difunctional or polyfunctional compound in steps a) and b) is different.

7) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in any of the preceding claims, characterized in that the ethylenically monofunctional compound in steps a) and b) is the same.

8) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in any of the preceding claims, characterized in that the ethylenically monofunctional compound in steps a) and b) is different.

9) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in any of the preceding claims, characterized in that the polymer selected from a polyesterpolyol, polyurethane and/or polyacrylate contains on average per molecule at least one free carboxyl group that originates from trimellitic acid or trimellitic anhydride.

10) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in any of the preceding claims, characterized in that the ethylenically monofunctional compound is selected from the group of the alkyl esters or hydroxyalkyl esters of acrylic or methacrylic acid.

11) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in claim 10, characterized in that the ethylenically monofunctional compound is vinyl acetate, vinyltoluene, styrene, acrylamide or an alkyl (meth)acrylate or hydroxyalkyl (meth)acrylate having from 1 to 18 carbon atoms in the alkyl radical.

12) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in claim 11, characterized in that the alkyl (meth)acrylate is selected from the group of lauryl acrylate, isobornyl (meth)acrylate, cyclohexyl (meth)acrylate, tert-butylcyclohexyl (meth)acrylate, benzyl (meth)acrylate, glycidyl (meth)acrylate, and trimethylcyclohexyl (meth)acrylate.

13) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in claim 11, characterized in that the alkyl (meth)acrylate is selected from the group of α-ethylhexyl (meth)acrylate, methyl (meth)acrylate, n-butyl (meth)acrylate, and tert-butyl (meth)acrylate.

14) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in claim 11, characterized in that the

hydroxyalkyl (meth)acrylate is selected from the group of 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, hexane-1,6-diol mono(meth)acrylate, and 4-hydroxybutyl (meth)acrylate.

15) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in any of the preceding claims, characterized in that the ethylenically difunctional or polyfunctional compound is selected from the group of the diacrylates, triacrylates and/or (meth)acrylic esters of polyfunctional alcohols.

16) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in claim 15, characterized in that the ethylenically difunctional or polyfunctional compound is allyl (meth)acrylate, hexanediol di(meth)acrylate, ethylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, butanediol di(meth)acrylate or trimethylolpropane tri(meth)acrylate.

17) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in any of the preceding claims, characterized in that the ethylenically monofunctional compound is in part a polyester or polyurethane having an acid number of less than 5, in particular less than 3, which contains on average per molecule up to one polymerizable double bond.

18) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in any of the preceding claims, characterized in that the ethylenically

difunctional or polyfunctional compound is in part a polyester or polyurethane having an acid number of less than 5, in particular less than 3, which contains on average per molecule at least 1.5 polymerizable double bonds.

19) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in any of the preceding claims, characterized in that of the polymers used in step a) during the polymerization the

- polyesterpolyol has a number-average molecular weight of between 700 and 5 000, with particular preference between 750 and 2 000; an acid number of between 35 and 150, with particular preference between 40 and 120; and an OH number of between 150 and 300, with particular preference between 220 and 280;
- polyurethane has a number-average molecular weight of between 700 and 5 000, with particular preference between 750 and 2 500; an acid number of between 30 and 120, with particular preference between 40 and 80; and an OH number of between 150 and 300, with particular preference between 220 and 280; and/or

  polyacrylate has a number-average molecular weight of between 2 500 and 20 000, with particular preference between 4 000 and 10 000; an acid number of between 35 and 150, with particular preference between 40 and 125; and an OH number of between 100 and 250, with particular preference between 150 and 200.

20) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in any of the preceding claims, characterized in that the polyesterpolyol used in step a) during the polymerization contains no

polymerizable double bond and is obtainable from the reaction of at least one polycarboxylic acid without a polymerizable double bond with at least one polyol without a polymerizable double bond.

21) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in any of claims 1 to 19, characterized in that the polyesterpolyol contains on average per molecule at least one polymerizable double bond and is obtainable from the reaction

i) of at least one polycarboxylic acid without a polymerizable double bond with at least one polyol having at least one polymerizable double bond;

ii) of at least one polycarboxylic acid having at least one polymerizable double bond with at least one polyol without a polymerizable double bond; or

iii) of at least one polycarboxylic acid having at least one polymerizable double bond with at least one polyol having at least one polymerizable double bond.

22) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in claim 20 or 21, characterized in that the polycarboxylic acid without a polymerizable double bond is selected from the group of

- succinic acid, glutaric acid, adipic acid, azelaic acid, terephthalic acid, phthalic acid, isophthalic acid, endomethylenetetrahydrophthalic acid, 1,2-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, dodecanedioic acid, dodecanedicarboxylic acid;
- dimeric and polymeric fatty acids, and trimellitic acid;

and the possible anhydrides thereof.

23) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in any of the preceding claims 20 or 22, characterized in that the polyol without a polymerizable double bond is selected from the group of

- ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, hexaethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2-dimethylpropanediol, 2,2,4-trimethylpentanediol, 1,3-dimethylolcyclohexane, 1,4-dimethylolcyclohexane, hydroxypivalic acid neopentyl glycol monoester, dimethylolpropionic acid, and perhydrogenated bisphenol A;
- trimethylolpropane and glycerol; and
- pentaerythritol, dipentaerythritol, and di(trimethylolpropane).

24) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in any of claims 21 to 23, characterized in that the polycarboxylic acid having at least one polymerizable double bond is selected from the group of maleic acid, fumaric acid, itaconic acid, citraconic acid, and aconitic acid, and the possible anhydrides thereof.

25) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in any of claims 21 to 24, characterized in that the polyol having at least one polymerizable double bond is selected from the group

- of 1,4-butenediol, allyl dimethylolpropionate, vinyl dimethylolpropionate, trimethylolpropane monoallyl ether, glycerol monoallyl ether;
- the adducts of allyl glycidyl ether or glycidyl (meth)acrylate with a polyester containing a carboxyl group; and
- the adducts of allyl glycidyl ether or glycidyl (meth)acrylate with dimethylolpropionic acid.

26) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in any of claims 19 to 25, characterized in that the polyesterpolyol has been modified by at least one monocarboxylic acid selected from the group of the saturated or unsaturated, isolated or conjugated, linear or branched fatty acids and of benzoic acid or crotonic acid.

27) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in claim 26, characterized in that the fatty acid has from 5 to 22 carbon atoms and in particular is linoleic acid, oleic acid, soya fatty acid, isononanoic acid or isostearic acid.

28) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in any of the preceding claims, characterized in that the crosslinker is an amino resin or a polyisocyanate.

29) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in claim 28, characterized in that the amino resin is a melamine resin.

30) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in claim 28, characterized in that the polyisocyanate is selected from the group of 1,3-bis(1-isocyanato-1-methylethyl)benzene (TMXDI, m-tetramethylxylylene diisocyanate), (4,4'-dicyclohexylmethane diisocyanate, Desmodur W), isophorone diisocyanate (IPDI, 3,5,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane), and 2,4,6-trioxo-1,3,5-tris(6-isocyanatohexyl)hexahydro-1,3,5-triazine (Desmodur N3300).

31) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in claim 28 or 30, characterized in that the polyisocyanate has been hydrophilically modified.

32) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in any of the preceding claims, characterized in that the degree of neutralization of the polyesterpolyol throughout the preparation process is between 30 and 100%, in particular between 50 and 80%.

33) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in any of the preceding claims, characterized in that the polymerization corresponding to step a) is conducted as an emulsion polymerization using a nozzle jet disperser or a water jet emulsifier.

34) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in any of the preceding claims, characterized in that the polymerization corresponding to step a) is conducted as a redox

polymerization using ascorbic acid, iron(II) sulfate, and at least one hydroperoxide.

35) The polymer microparticle dispersed in an aqueous phase and with a fully crosslinked exterior, as claimed in any of the preceding claims, characterized in that it is converted into a water-free form.

36) The use of polymer microparticles dispersed in an aqueous phase, as claimed in any of the preceding claims, for aqueous or solventborne coating compositions.

37) The use as claimed in claim 36 for aqueous or solventborne basecoat materials, effect basecoat materials or clearcoat materials in the automobile industry.

38) The use as claimed in claim 36 or 37 for aqueous or solventborne pigment formulations.